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Microarticle

The Gibbs method in thermodynamics of heterogeneous substances carrying electric charges

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ABSTRACT

We combine Gibbsian method thermodynamic method for heterogeneous systems with electrostatics. The substances under study are those able to accumulate free (i.e., not dipolar) electric charges. We announce several key formulas related to the first and second energy variations for these macroscopic heterogeneous systems.

Introduction

The systems carrying electric charges are widespread in nature and applications. Variational principles and methods play a key role in modeling these systems, and they have been developed for a couple of centuries (see very instructive publications [1–4]). Nonetheless, even a quick glance at the literature shows that the variational approach is far off to be exhaustive. In particular, in terms of calculus of variations, all the studies are based on the analysis of first energy variations (i.e., analysis of ponderomotive forces and conditions of equilibriums.) The analysis of the second variation, the cornerstone of the stability analysis, is not even touched. Moreover, the very expressions of the second energy variations still remain unknown (the publications [5–8] and references therein are very rare exceptions from this rule.) In this short note, we publish corresponding results relating to the simplest systems: the systems accumulating and carrying free electric charges. To make the presentation as simple as possible we limit ourselves with incompressible substances and ignore polarization effects.

Formalization of the Gibbs method

Many, even incompatible, interpretations of Gibbs classics [1] are known. All of them have their strong features and weaknesses. We follow the footsteps of Gibbs [1] in the interpretation of [9].

Consider a rigid body with distributed electric charges. Let the $\rho(z)$ and $\eta(z)$ be the distributions of densities per unit volume of the free distributed electric charges and entropy, respectively. We assume that these distributions can vary arbitrarily provided that their integral amounts remain fixed:

$$\int_\Omega d\Omega \rho(z) = Q, \tag{1}$$

$$\int_\Omega d\Omega \eta(z) = H \tag{2}$$

We assume that the total energy of the system E_{tot} is comprised of the total internal energy internal E_{int} and total electrostatic energy; thus, the total energy is given by the integral

$$E_{tot} = E_{int} + E_{elec} = \int_\Omega d\Omega U(\rho,\eta) + \frac{1}{2}\int_\Omega d\Omega \int_\Omega d\Omega^* \frac{\rho(z)\rho(z^*)}{|\vec{z}-\vec{z}^*|} \tag{3}$$

where $U = U(\rho,\eta)$ is the simplest model of the internal energy density.

Using the standard method of the Lagrange indefinite multipliers, we arrive at the unconditional variational problem for the functional Φ

$$\Phi = \int_\Omega d\Omega [U(\rho,\eta) - \Lambda\rho - \Gamma\eta] + \frac{1}{2}\int_\Omega d\Omega \int_\Omega d\Omega^* \frac{\rho(z)\rho(z^*)}{|\vec{z}-\vec{z}^*|} \tag{4}$$

where Λ and Γ are indefinite Lagrange multipliers.

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First variation and equilibrium equations

The first variation of the functional Φ reads

$$\delta\Phi = \int_\Omega d\Omega \left[\left(U_\rho - \Lambda + \int_\Omega d\Omega^* \frac{\rho(z^*)}{|\vec{z} - \vec{z}^*|} \right) \delta\rho + (U_\eta - \Gamma)\delta\eta \right] \tag{5}$$

Separating the independent variations, we arrive at the following conditions of the bulk equilibrium:

$$U_\rho + \int_\Omega d\Omega^* \frac{\rho(z^*)}{|\vec{z} - \vec{z}^*|} = \Lambda \tag{6}$$

and

$$U_\eta = \Gamma \tag{7}$$

Thus, we arrive at the system of 4 equations: 3 integral Eqs. (1), (2) and (6), and 1 - algebraic (7), with respect to 4 unknowns: 2 spatial functions $\rho(z)$ and $\eta(z)$, and 2 unknown constants Λ and Γ. No boundary conditions are necessary for this system.

Second variation and stability conditions

By varying formula (5) one more time in the vicinity of equilibrium configuration, we arrive at the following formula of the second variation:

$$\delta^2\Phi = \int_\Omega d\Omega \left[U_{\rho\rho}(\delta\rho)^2 + 2U_{\rho\eta}\delta\eta\delta\rho + U_{\eta\eta}(\delta\eta)^2 + \int_\Omega d\Omega^* \frac{\delta\rho(z)\delta\rho(z^*)}{|\vec{z} - \vec{z}^*|} \right] \tag{8}$$

For stability, the second quadratic form should be nonnegative for the arbitrary variations satisfying the linear bulk constraints:

$$\int_\Omega d\Omega\delta\rho(z) = 0, \quad \int_\Omega d\Omega\delta\eta(z) = 0 \tag{9}$$

Heterogeneous systems with 2 nondeformable solids exchanging free electric charges

Practically the same analysis can be applied to heterogeneous systems, in which 2 different solids have a common boundary Σ, through which electric charges can freely move in both directions but are not able to change the a priori fixed position of the interface Σ, neither in space nor with respect to the bodies (this assumption, basically prohibits the possibility of phase transformations between the solid phases [9]). The only change that must be taken into account is the internal energy function $U(\rho, \eta)$, which now can be different for 2 different solids. Following changes, then required in the system (1)–(9): the domain Ω should be replaced with the combined domain $\Omega \to \Omega_1 \cup \Omega_2$; Eqs. (6) and (7) should be replaced with

$$U^1_\rho + \int_{\Omega_1 \cup \Omega_2} d\Omega^* \frac{\rho(z^*)}{|\vec{z} - \vec{z}^*|} = \Lambda, \quad z^i \ni \Omega_1, \tag{10}$$

$$U^2_\rho + \int_{\Omega_1 \cup \Omega_2} d\Omega^* \frac{\rho(z^*)}{|\vec{z} - \vec{z}^*|} = \Lambda, \quad z^i \ni \Omega_2$$

and

$$U^1_\eta = U^2_\eta = \Gamma, \quad z^i \ni \Omega_1 \cup \Omega_2 \tag{11}$$

Further modifications required for the case for the models with electric charges concentrated on the interface or for the models with mobile interfaces. These cases will be considered elsewhere.

Conclusion

For the heterogeneous systems (in the sense of Gibbs [1]) we suggest a formulation of thermodynamics generalizing the classical Gibbs variational principles. We presented explicit formulas of the first and second variations that open the venue to mathematically consistent studies of equilibrium and stability conditions for such systems.

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